

**Final**

**Behavior of Dense Non-Aqueous Phase Liquids  
(DNAPL) in Porous and Fractured Media**

**With Review and Recommendations for Ground  
Water Remediation at the Rocky Flats  
Environmental Technology Site**

**Tim Reeves  
SAIC  
14062 Denver West Parkway, Suite 202  
Golden, Colorado 80401**

**Thomas Beardon  
SAIC  
14062 Denver West Parkway, Suite 202  
Golden, Colorado 80401**

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## 1.0 Introduction

The Rocky Flats Environmental Technology Site (RFETS) is a contractor-operated facility owned by the United States Department of Energy (DOE). The plant is located approximately 16 miles (26 kilometers) northwest of Denver, Colorado and comprises approximately 6,550 acres (2,652 hectares). Until 1992, the plant was operated as a weapons research, development and production complex. Weapons components were manufactured from plutonium, beryllium, and stainless steel and shipped to other facilities for assembly. The former Rocky Flats Plant was renamed RFETS in 1994 to more formally reflect its new mission in environmental restoration, research and technology development.

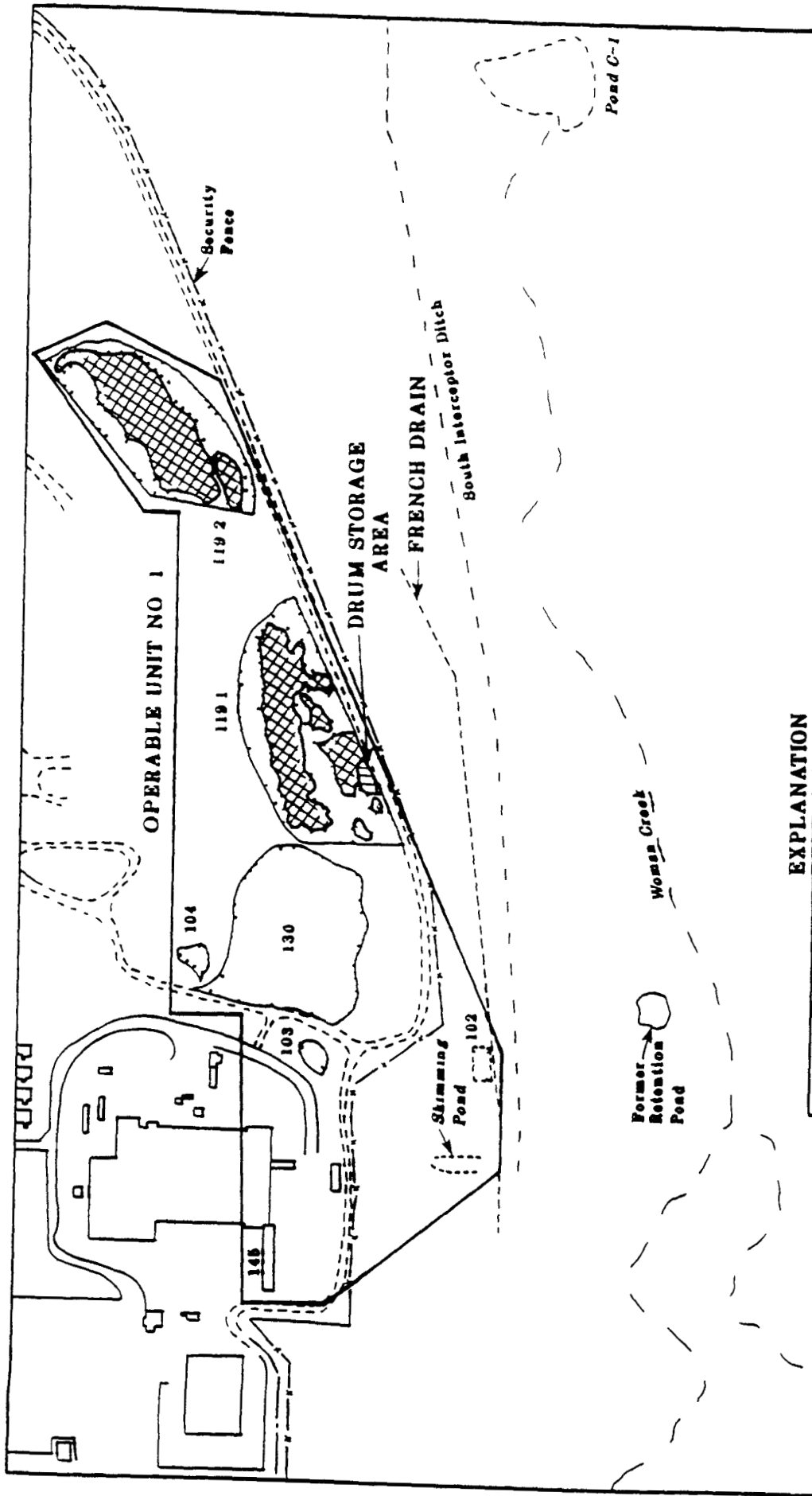
The weapons production process generated a variety of wastes, some of which were contaminated by radionuclides, or RADs. Past waste management practices, primarily on-site storage and disposal activities, resulted in areas where soil, surface water and ground water were contaminated by hazardous and/or radioactive wastes. Areas where wastes had been previously stored or disposed of at the Rocky Flats Plant were identified by an Environmental Restoration Program as areas where environmental contamination could potentially exist (DOE, 1986). Of particular concern is contamination of ground water by chlorinated solvents. This review and recommendation document focuses on Operable Unit 1 (OU 1), the 881 Hillside, as a case study. The document applies, however, to ground water contamination in OU 2, the 903 Pad, Mound and East Trenches, and OU 4, the Solar Ponds. The primary chlorinated solvents that are contaminants at these OUs are carbon tetrachloride ( $\text{CCl}_4$ ), tetrachloroethylene (PCE), and trichloroethylene (TCE). These contaminants are considered in a class of compounds known as Dense Non-Aqueous Phase Liquids (DNAPLs).

OU 1 was designated as a high-priority site because preliminary investigations indicated that there was elevated levels of chlorinated solvents/volatile organic compounds (VOCs) in ground water and because of its proximity up-gradient of Woman Creek, a surface water drainage. The ground water contamination, primarily consisting of PCE, TCE, and  $\text{CCl}_4$ , appeared to be associated with two IHSSs designated 119 1 and 119 2 (Multiple Solvent Spill Sites). These IHSSs were used for the storage of scrap metal and drums from approximately 1968 through 1972 (DOE 1992). The drums were suspected to contain unknown amounts and types of waste solvents, possibly contaminated by radionuclides and the scrap metal was potentially contaminated with residual cutting oils and/or hydraulic coolants (DOE 1992).

An Interim Measure/Interim Remedial Action (IM/IRA) plan (DOE 1990) was developed to prevent further contamination until the RCRA Facility Investigation/Remedial Investigation (RFI/RI) and Corrective Measures Study/Feasibility Study (CMS/FS) could be completed for OU 1. The IM/IRA plan essentially consisted of containment and "Pump-and-Treat" operations to remediate the contaminated ground water. The IM/IRA was constructed at OU 1 in 1992 and consisted of a French Drain, a ground water Extraction Well and a Water Treatment Facility. The IM/IRA and the operation of the water treatment system is described in more detail in Section 3.0 of this report. Figure 1.1 shows the location of IHSSs, the drum and scrap metal storage areas, and the French Drain at OU 1.

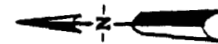
Capital costs to implement the OU 1 IM/IRA were approximately \$10 million plus an additional \$600 thousand were incurred to conduct treatability studies and for design. Annual operating costs have been approximately \$800 thousand.

"Pump-and-treat" technologies for the restoration of contaminated ground water were largely implemented after the passage of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) in 1980 and passage of amendments to the Resource Conservation and Recovery Act (RCRA) in 1984. Between 1982 and 1992, 73 percent of Superfund sites with contaminated ground water had cleanup agreements specifying the use of pump-and-treat for restoration (National Research Council 1994). Recent studies by the Environmental Protection Agency (EPA) as well as other independent researchers have evaluated the effectiveness of pump-and-treat technologies (EPA 1989a, EPA 1989b, Mercer et al. 1990, Mackay and Cherry 1989, Doty and Travis 1991, and EPA 1992, and others). These studies consisted of technical reviews of several Superfund sites where pump-and-treat systems were being applied for remediation. The general conclusion of these studies is that pump-and-treat systems are unable to remove enough contamination to restore the ground water to drinking water standards, or that achievement of these standards will require an extremely long time (i.e., decades to centuries). These studies created a general concern among government agencies, scientists, environmental groups and the public that large amounts of money are being applied to ground water restoration, yet clean up goals (i.e., drinking water standards) are not being achieved. As a result of these concerns, the National Research Council initiated a comprehensive study to review ground water clean up systems. The results of this study and the recommendations of the National Research Council have recently been reported (NRC 1994). As a part of the study, the NRC evaluated 77 Superfund sites where pump-and-treat was being applied for restoration of ground water. Of the 77 total sites reviewed, 69 sites have not achieved clean up goals, and of 42 DNAPL contaminated sites, none had achieved clean up goals.



### EXPLANATION

INDIVIDUAL HAZARDOUS SUBSTANCE SITE (IHSS) AND  
IHSS DESIGNATION, DASHED WHERE DISTURBED DURING  
CONSTRUCTION OF FRENCH DRAIN  
ACTUAL SCRAP METAL AND DRUM STORAGE AREAS IN  
IHSS 119 BASED ON AERIAL PHOTOGRAPHS  
ACTUAL DRUM STORAGE AREA IN IHSS 119 BASED ON  
AERIAL PHOTOGRAPHS



U S DEPARTMENT OF ENERGY  
Rocky Plate Environmental Technology Site  
Golden Colorado

881 HILLSIDE AREA  
OPERABLE UNIT NO 1

Figure 11  
Individual Hazardous  
Substance Site Locations



This report was requested by the DOE Rocky Flats Field Office (RFFO) Environmental Restoration Organization as a result of the recent information and guidance published by the National Research Council and because of newly published research concerning the behavior of DNAPLs in the subsurface. The purpose of this paper is to briefly outline the problems and factors associated with the remediation of DNAPLs in ground water because this type of contamination has been identified at OU 1, OU 2, and OU 4 at RFETS. The DOE further requested that recommendations be made relative to operation of the OU 1 IM/IRA. The specific objectives of this paper are to

- Outline factors associated with the fluid behavior of Dense Non-Aqueous Phase Liquids (DNAPLs) in saturated and unsaturated media (vadose zones) that affect ground water restoration
- Review the effectiveness of pump-and-treat operations as a treatment alternative to remediate ground water sites contaminated by DNAPL
- Technically review the current operations of the OU 1 IM/IRA pump-and-treat operations being conducted for the Operable Unit No. 1 (OU 1) to provide as an example for RFETS

Section 2.0 of this paper briefly outlines the properties and behavior of Dense Non-Aqueous Phase Liquids in porous and fractured media. This section also defines many of the important geohydrologic factors associated with this type of contamination. Section 3.0 of this report specifically outlines the factors associated with pump-and-treat and enhanced pump-and-treat technologies to remediate DNAPL contamination in ground water. A review of the OU 1 IM/IRA operations is contained in Section 4.0 with recommendations for that operation.

## 2.0 Fluid Properties and Behavior of DNAPLs in Porous and Fractured Media

A large class of organic compounds, known as Non-Aqueous Phase Liquids (NAPLs), have become common contaminants in ground water in many industrialized areas. NAPLs are generally immiscible with water, meaning that the two compounds will form separate phases when mixed together. NAPLs are generally broken down into two broad classes known as Dense NAPLs (DNAPLs) or Light NAPLs (LNAPL) depending on their relative density to water. Common LNAPLs are gasoline, diesel, or BTEX and will float on top of water. DNAPLs are heavier than water and, since they are immiscible, will migrate below a water table and remain as a separate free phase in the subsurface environment. Common DNAPLs are chlorinated solvents, creosote, dense hydrocarbons, and PCB oils. Densities of some DNAPLs that are commonly associated with ground water contamination are listed in Table 2.1.

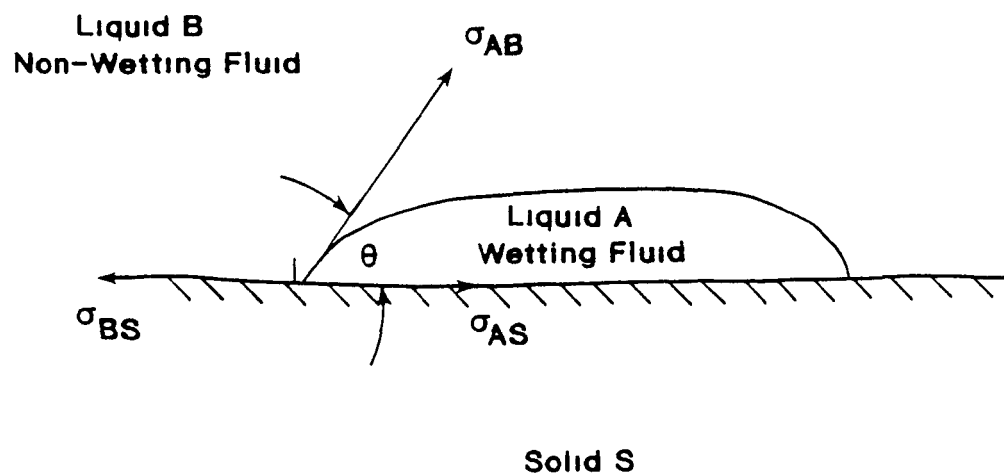
**Table 2.1 Densities of common DNAPLs in relation to pure water.**

Compound	Density (g/L)	Temperature °C
tetrachloroethylene	1630	20
trichloroethylene	1470	20
carbon tetrachloride	1594	20
1,1-dichloroethane	1170	20
coal tar	1028	7-2
aroclor 1242	1734	25
water	1000	4

A general understanding of the fluid properties of DNAPLs with respect to water and air are extremely important when describing DNAPL behavior in the subsurface and in ultimately developing or evaluating technologies to remediate these contaminants. The most important fluid properties relative to ground water contamination is interfacial tension. A secondary property, which is a function of interfacial tension, is the wettability of a fluid. A detailed discussion of interfacial tension and the wettability of fluids with respect to porous materials is given by Kueper et al. (1993) and Kueper and McWhorter (1991) and is summarized below.

Wettability is a physical property of two pure immiscible fluids and a solid surface. One fluid will preferentially "wet" a solid surface with respect to the other fluid. The wettability of liquids relative to air is frequently measured by placing a drop of the liquid on the surface of the solid. The wettability of the fluid is measured by the contact angle established between the solid and a drop of the discontinuous fluid (Figure 2.1). The wettability is quantified by the contact angle of the interface between the liquid and the solid. By definition, the fluid is wetting with respect to the

## WETTABILITY



- $\theta$  = Contact Angle
- Wetting Fluid: Fluid through which  $\theta < 90^\circ$
- Non-Wetting Fluid: Fluid through which  $\theta > 90^\circ$
- Perfectly Wetting Fluid:  $\theta = 0^\circ$

Figure 2 1 Illustration of the measurement for wettability (Kueper 1994)

solid if the contact angle is less than 90 degrees. The fluid is non-wetting if the contact angle is greater than 90 degrees. Table 2.2 outlines wetting and non-wetting fluids with respect to most geologic materials as the solid (Kueper 1994).

Table 2.2 Typical Qualitative Wettability of Organic Liquids (including DNAPLs) in a Porous Medium Saturated with Air or Water

System	Wetting Fluid	Non-wetting Fluid
Air/Water	Water	Air
Air/Organic	Organic	Air
Water/Organic	Water	Organic

The general rule for almost all soils, rocks and geologic materials is that water is wetting with respect to both organic liquids and air, and that organic liquids are wetting with respect to air. In the vadose zone, DNAPL wets the surface of the porous media (soil) because it is wetting with respect to air. In the saturated zone, a DNAPL is usually the non-wetting fluid because water is more strongly attracted to soil and rock than the organic material. Much of the characteristic behavior of DNAPLs, and the technical problems associated with their remediation below a water table, is because DNAPL is the non-wetting fluid with respect to water in geologic materials.

Interfacial tension exists at the interface of any two immiscible fluids and arises because of interactions between the two chemical species at the interface. A high degree of interfacial tension will exist between two fluids that are very immiscible. If no interfacial tension exists, the fluids are miscible and will not form separate phases. DNAPLs generally have a high interfacial tension with respect to water. Because of interfacial tension, the wetting fluid exhibits a concave surface on the interface with the non-wetting fluid. The forces of interfacial tension create a pressure discontinuity across the curved surface between the fluids (Figure 2.2). The difference between these two pressures is called the "capillary pressure". Capillary pressure as defined by Bear (1972) is the pressure difference between the non-wetting fluid and the wetting fluid.

$$P_C = P_{NW} - P_W \quad (2.1)$$

where  $P_C$  is the capillary pressure,  $P_{NW}$  is the pressure of the non-wetting fluid and  $P_W$  is the pressure of the wetting fluid. In an uncontaminated vadose zone containing air, water and soil, water is the wetting fluid with respect to air. The capillary pressure in a given pore space is the

difference between the air pressure, which is usually atmospheric, and the pressure exhibited by the water. In this case, the capillary pressure is highly positive and the water is said to be held in the soil by capillary tension or "capillarity". In a saturated system with two immiscible phases, DNAPL and water, the capillary pressure is the difference in the pressure of the DNAPL (the non-wetting fluid) and the pressure of the water (the wetting fluid).

A large variety of pore sizes and shapes exist in any given porous media or in fracture sizes in a fractured media. The degree of porosity and its homogeneity is largely a function of the geologic origin of the media, the variation of particle sizes, and how particles are sorted. Different pores or fractures will have different sizes of throat openings or "apertures". In order for a non-wetting fluid to enter a pore or fracture, a specific pressure must be exceeded. This pressure is commonly referred to as the "entry pressure" (Kueper et al 1993, Kueper and McWhorter 1991, McWhorter and Sunada 1977) and is governed by the size and geometry of the aperture opening. In order for a DNAPL to enter a pore or fracture filled with water, the capillary pressure must exceed the entry pressure of the pore aperture so that the DNAPL-water interface can physically penetrate the aperture (Kueper and McWhorter 1991). In general, larger pores with larger aperture openings have lower entry pressures and smaller pores with smaller aperture openings have higher entry pressures. Kueper and McWhorter (1991) show that the entry pressure for a perfectly circular aperture can be defined by

$$P_E = \frac{4 \sigma \cos \theta}{e}$$

where  $P_E$  is the entry pressure of the aperture,  $\sigma$  is the interfacial tension between DNAPL and water,  $\theta$  is the contact angle measured through the wetting phase, and  $e$  is the diameter of the aperture opening. Once the entry pressure is exceeded, the non-wetting fluid will displace the wetting fluid from the pore or fracture. The concept that capillary pressures, defined as the pressure of the water subtracted from the pressure of the DNAPL, must exceed the entry pressures for pores and fractures is the most important factor governing the migration and distribution of DNAPLs in the subsurface. It is also the main reason why residual DNAPL in the subsurface can not be easily moved hydraulically (i.e. by pumping or injecting water to manipulate the gradient).

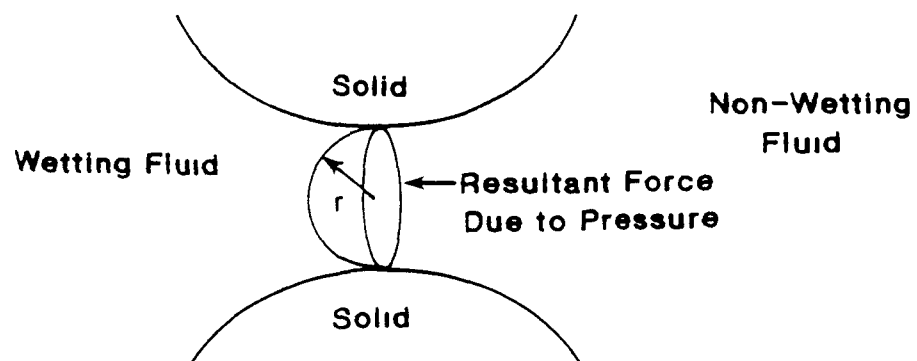


Figure 2 2 Idealized intertace between a wetting and non-wetting fluid in porous media Adapted from McWhorter and Sunada (1977)

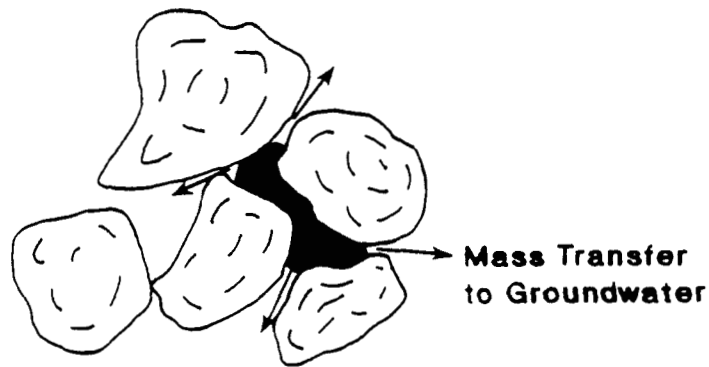
As DNAPL enters a porous media, it will migrate and follow the largest and most preferential flow paths where the entry pressures are less than the capillary pressures of the DNAPL-water system. In the partially saturated vadose zone migration paths are extremely convoluted because DNAPL is wetting with respect to air and non-wetting with respect to water. As DNAPL migrates through a porous media, small volumes of disconnected residual are trapped or snapped off in pores where an equilibrium is established between the DNAPL-water interface at the pore throat (Kueper et al 1993). This residual, commonly referred to as globules or ganglia, is essentially held in the pore spaces or fractures by capillary forces. Kueper et al (1993) indicate that the degree of residual globules which will become trapped is a function of several factors, including pore geometry, aspect ratio, pore size distribution, and hydraulic gradient. Depending on these factors, it follows that the larger the number of pores and aperture openings that are invaded by non-wetting fluid the larger the number of pores in which residual globules will be left behind (Kueper et al 1993). Figure 2.3 illustrates residual DNAPL in pore spaces in both the vadose zone and saturated zones. This figure also illustrates the concave and convex curvature of the interfaces between the wetting and non-wetting phases, respectively.

When migrating DNAPL comes in contact with lenses or micro-lenses of lower permeability (i.e. where the entry pressures are higher) it moves laterally, sometimes forming pools or fingers that break off at the edge of the lens. It is important to note that lateral migration and pooling is not a function of the reduced hydraulic conductivity in these zones. Rather, it is because the height of the continuously connected migrating DNAPL is not sufficient to raise capillary pressures above the entry pressures for these lenses. In studying the behavior of PCE migration in a seemingly homogenous media, Poulsen and Kueper (1992) noted that residual was distributed at the scale of millimeters in response to the micro-scale bedding planes and lenses. Small DNAPL pools may form on the top of lateral bedding structures or on bedrock or fractured bedrock. Similar to the case for low permeability lenses, DNAPL will not enter fractures in bedrock unless the pool height is sufficient to raise the DNAPL-water capillary pressure above the entry pressure of the fracture. A typical conceptual model for a DNAPL spill is depicted in Figure 2.4.

Residual DNAPL, occurring either as globules in pores or as small pools along bedding planes, is essentially immobile because it is held by capillary forces. DNAPL will not flow in a two-phase, DNAPL-water, system. However, hydraulic manipulation of the water, by pumping and/or injecting, can slightly change the water pressure and thus the capillary pressure across the DNAPL-water interface. Although it is difficult to significantly affect established capillary pressures, this can cause DNAPL to slightly migrate or spread. For example, pumping of water in a pump-and-treat system would reduce the water pressure in the capture zone of a well. An evaluation of

## Residual DNAPL - Pore Scale

### Below Water - Table (Porous Media)



### Above Water - Table (Porous Media)

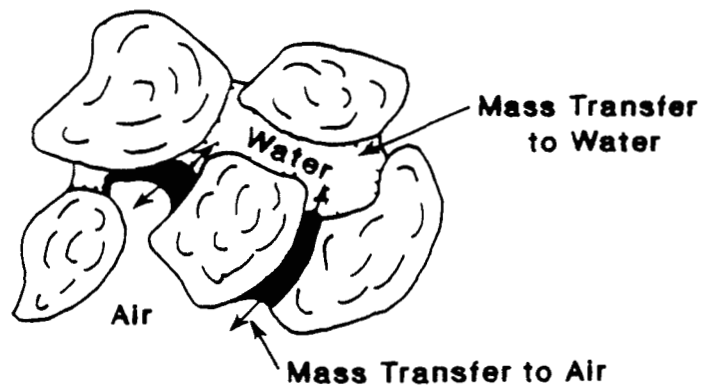


Figure 2.3 Residual DNAPL in pore spaces in both the vadose zone and saturated zones. The vadose zone is a three-phase system consisting of air, water, and DNAPL. The saturated zone is a two-phase system consisting of water and DNAPL (Kueper 1994).



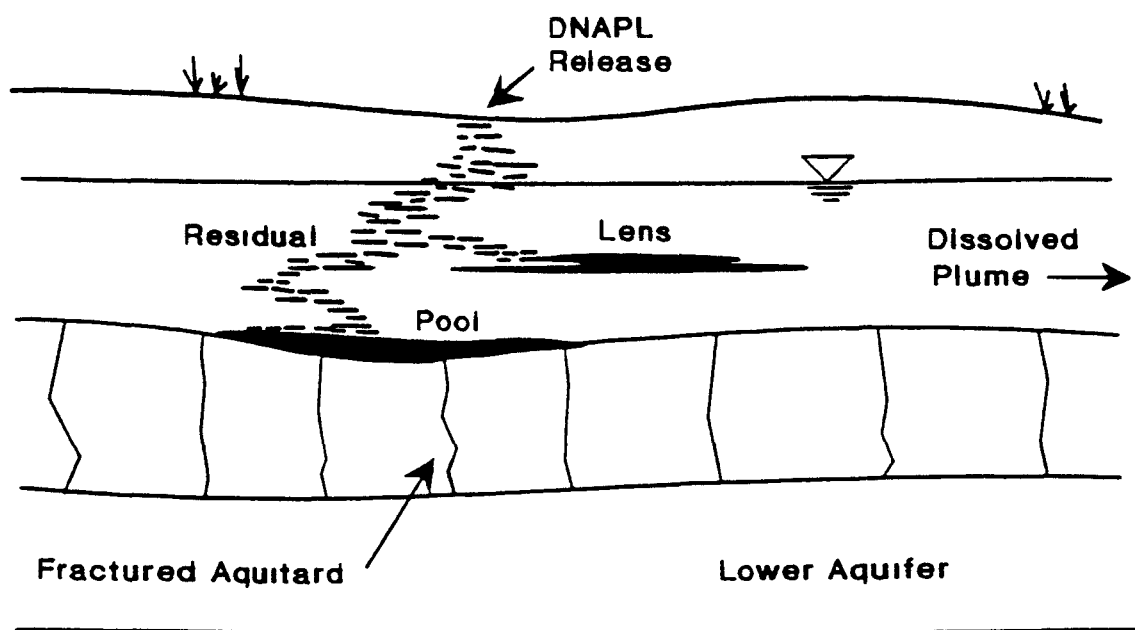


Figure 2.4 Conceptual model of a DNAPL spill into a geologic system

Equation 2.1, however, shows that reducing the water pressure would increase the capillary pressure across any DNAPL-water interface. Portions of the DNAPL would migrate to smaller pores spaces or enter smaller fractures where the capillary pressure now exceeds the entry pressure. Cherry (1994) and Kueper and McWhorter (1991) note that pumping in a fractured lower aquifer below pooled or residual sources can cause DNAPL to enter fractures or an additional aquifer where contamination did not previously exist.

In summary, DNAPLs are immiscible, non-wetting fluids with respect to water which combine with the natural heterogeneity in the properties of aquifers to make ground water remediation extremely difficult. Residual free-phase DNAPL is held in both porous and fractured media by capillary forces, making it essentially immobile with respect to the hydraulic potentials acting on the flow of ground water. For this reason, pump-and-treat systems cannot extract the free-phase residual DNAPL from an aquifer system, but only the ground water containing the dissolved phase of the contaminant. The solubility of most DNAPLs in water is very low and only a small amount of the total mass of the contaminant will be present in the dissolved phase. The remaining residual DNAPL is likely to remain in the soil and contaminant any ground water influent to the contaminated zone.

### 3.0 Review of Pump and Treat Technologies for Remediation of DNAPLs

The National Research Council (NRC) has recently conducted an in-depth study and review of pump-and-treat systems for ground water restoration. The NRC set up the Committee on Ground Water Cleanup Alternatives with recognized scientists, researchers, and government officials in the areas of environmental engineering, geohydrology, chemistry, epidemiology, environmental economics, and environmental law and policy. The committee was formed under the NRC's Water Science and Technology Board and the Board on Radioactive Waste Management. The committee produced a comprehensive report which thoroughly evaluates and reviews pump-and-treat technologies for ground water restoration (NRC 1994). The report further provides in-depth discussions of alternative enhancements to pump-and-treat systems, such as bioventing and soil vapor extraction, and provides strong recommendations regarding the application of clean up standards by the EPA in relation to the technological state-of-the-art in ground water restoration technology. The objectives of the NRC study were 1) to review the performance of existing pump-and-treat systems, 2) to determine the performance capabilities of innovative cleanup technologies, 3) to determine the scientific and technological limits to restoring contaminated ground water, 4) to evaluate and consider public health and economic consequences of ground water contamination, and 5) to provide advice on whether changes in national ground water policy are needed to better reflect the limits of current technology.

The results of this study and the recommendations of the National Research Council have recently been reported (NRC 1994). As a part of the study, the NRC evaluated 77 Superfund sites where pump-and-treat was being applied for restoration of ground water. Of the 77 total sites reviewed, 69 sites have not achieved clean up goals, and of 42 sites where the contamination was from DNAPLs, none had achieved clean up goals. The eight sites where goals had been achieved were sites that had homogeneous aquifers, high hydraulic conductivities, and the contamination source was mobile (i.e. not easily sorbed to geologic media). One LNAPL site, a gas station, had achieved clean up goals where pump-and-treat was used to remediate ground water where gasoline had leaked from an underground storage tank.

Pump and treat systems are based on the simple theory that contaminated ground water is extracted from the subsurface and the extracted water is replaced by uncontaminated water. The uncontaminated water can be injected from the surface or be replaced through the natural flow of ground water. The extracted water is usually treated by a water treatment process where contaminants are removed or destroyed. As previously indicated, reviews of pump-and-treat systems have strongly indicated that these systems are largely unsuccessful in remediating ground

water to the required clean up goals, usually drinking water standards (EPA 1989a, EPA 1989b, Mercer et al 1990, Mackay and Cherry 1989, Doty and Travis 1991, EPA 1992, and NRC 1994) Travis and Doty (1990) questioned any application of pump-and-treat, given the high costs incurred and the poor record of these systems in achieving health based standards NRC (1994), however, indicated that some pump-and-treat/extraction well systems have been designed to strictly control the growth of a contaminated plume or prevent the outfall of contaminated ground water to surface sources They report that these systems are generally operated at much less cost than systems designed for remediation

The inability of pump-and-treat technologies to effectively remediate ground water is primarily due to geohydrologic factors and the specific properties of the contaminants Based on case studies, NRC (1994) illustrates that it becomes more difficult to remove contamination as geohydrologic conditions become more heterogeneous and fractured They further show that removal of contaminant mass is strongly affected by the degree that a contaminant becomes adsorbed to the surrounding soil and geologic matrix or if the contaminant is a Light or Dense NAPL Table 3 1 outlines the relative ease of remediation as a function of these factors as reported by NRC (1994) Although this table is only a simple qualitative assessment of complicated interactive geohydrologic and chemical properties, it effectively categorizes the potential for remediation success, given contaminant source and geohydrologic conditions It particularly illustrates the difficulty associated with remediating contamination by DNAPLs, such as those that occur at OU 1 and OU 2 at the RFETS

The fluid properties of DNAPLs and their behavior in the subsurface are detailed in Section 2 0 of this report In general, the behavior of DNAPLs as an immiscible, non-wetting fluid with respect to water combines with the natural heterogeneity in the properties of aquifers to make restoration extremely difficult Residual free-phase DNAPL is held in both porous and fractured media by capillary forces, making it essentially immobile with respect to the hydraulic potentials acting on the flow of ground water For this reason, pump-and-treat systems can not extract the free-phase residual DNAPL from an aquifer system but can only extract ground water containing the dissolved phase of the contaminant Unfortunately, the solubility of most DNAPLs in water is very low and only a small amount of the total mass of the contaminant will be present in the dissolved phase This physical system is further complicated by the fact that only small concentrations of dissolved DNAPL in water will still exceed health based drinking water standards For example, the Federal Maximum Contaminant Level for dissolved TCE in drinking water is 5 ppb It is for these combined reasons that DNAPL sites are often considered the most technically difficult and are often infeasible to restore

TABLE 3-1 Relative Ease of Cleaning Up of Contaminated Aquifers as a Function of Contaminant Chemistry and Hydrogeology (NRC 1994)

Hydrogeology	Contaminant Chemistry				
	Mobile, Dissolved (degrades/ volatilizes)	Mobile, Dissolved	Strongly Sorbed, Dissolved <sup>a</sup> (degrades/ volatilizes)	Strongly Sorbed, Dissolved <sup>a</sup>	Separate Phase LNAPL
Homogeneous, single layer	1 <sup>b</sup>	1-2	2	2-3	3
Homogeneous, multiple layers	1	1-2	2	2-3	3
Heterogeneous, single layer	2	2	3	3	4
Heterogeneous, multiple layers	2	2	3	3	4
Fractured	3	3	3	3	4

<sup>a</sup> "Strongly sorbed" generally indicates contaminants for which the retardation coefficient is greater than 10. A retardation coefficient of 10 indicates that at any given time, 10 percent of the contaminant is dissolved in the water and 90 percent is sorbed to the aquifer solids.

<sup>b</sup> Relative ease of cleanup, where 1 is easiest and 4 is most difficult.

Figure 3 1 shows a typical observed response to the remediation of a DNAPL site by a pump-and-treat technology. Dissolved contaminant concentrations in the aquifer tend to drop rapidly but the rate of removal drastically declines. Remediation of the aquifer generally becomes asymptotic at some level above the remediation goal with continued progress towards permanent restoration extending for an extremely long time. It has also been observed that dissolved concentrations often return to original high levels if pumping ceases.

These observed effects are primarily caused by several interacting factors. Ground water flow toward an extraction well will follow paths of higher permeability, flushing these zones of dissolved contamination. Dissolved contamination in zones of lower permeability primarily transfers to areas of clean water by diffusion. Furthermore, as dissolution to the ground water progresses, the size and surface area of trapped globules or lenses of residual DNAPL becomes smaller. As pump-and-treat progresses, the remaining mass of residual DNAPL occurs in the areas of continually less preferential flow and with less surface area exposed to water for dissolution to occur. The transfer of mass from the free-phase DNAPL to the dissolved phase becomes increasingly dependent on diffusive processes rather than advective processes. Diffusion is a much slower physical process, thus significantly extending treatment time.

The same asymptotic response illustrated in Figure 3 1 has also been observed when other technologies, such as Soil Vapor Extraction (SVE) or bioremediation, have been applied for the remediation of NAPLs. In SVE, the porous media is flushed with air using both injection and extraction systems. The theory of SVE is that contaminant mass, occurring in the vapor phase, is removed from the system to allow more of the contaminant to volatilize from the trapped residual source. SVE has primarily been used at sites with LNAPL contamination, where the contamination source primarily occurs on top of the water table, or to treat residual Light or Dense NAPLs in the vadose zone. In cases where residual DNAPL occurs below the water table, the area must be dewatered using extraction wells prior to initializing a SVE system. Unfortunately, SVE is subject to the same limitations as pump-and-treat systems for ground water. The air flow will primarily follow the zones of highest permeability missing DNAPL residual. Diffusion will become the main mechanism for transfer of contaminant mass from zones of lower gas permeability. As previously indicated, this is an extremely slow process.

In situ bioremediation and the use of surfactants also exhibit the same problems associated with geologic heterogeneity that occur in conventional pump-and-treat and SVE systems. The injection of surfactants or microorganisms and their essential nutrients will only occur along preferential

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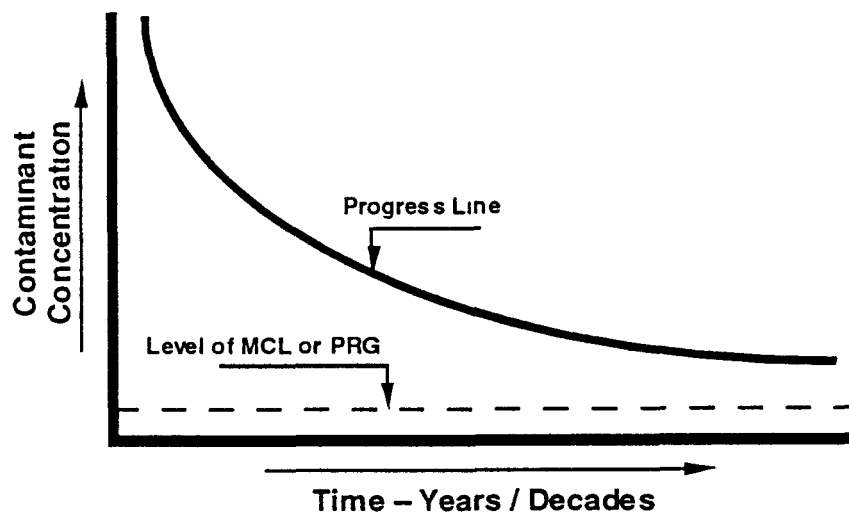


Figure 3 1      Conceptual model of the typical observed response to the remediation of a DNAPL site by a pump-and-treat or an enhanced pump-and-treat technology

flow paths It becomes extremely difficult to successfully deliver the necessary concentrations of the reagent or of the microorganisms to the low permeable zones where significant immobile DNAPL is present



## **4.0 Operation of the OU 1 Interim Measure/Interim Remedial Action**

### **4.1 Background of IM/IRA**

In 1989, DOE proposed an Interim Measure/Interim Remedial Action (IM/IRA) to minimize the release of hazardous substances from the 881 Hillside area while the assessment process and selection of the final remedial action were being conducted. The IM/IRA was designed to prevent potentially contaminated ground water from reaching Woman Creek. Woman Creek is a surface water drainage which eventually outfalls to Standely Lake, an off site water supply.

The IM/IRA consisted of the construction of an underground drainage system called a French drain, an extraction well, and a water treatment facility to treat contaminated ground water. The 1450-foot-long French drain was designed to intercept alluvial/colluvial ground water flow from the 881 Hillside Area, and the extraction well was installed near the area of known contamination in IHSS 119.1. Collected ground water is transferred to an on-site treatment facility in Building 891 for removal of volatile organics (VOCs), uranium, and metals. After treatment and testing, the water is released on-site into the South Interceptor Ditch. Water collected from this ditch then undergoes a secondary analysis prior to release from the site. Ground water treatment began in May of 1992.

Capital costs to implement the OU 1 IM/IRA were approximately \$10 million plus an additional \$600 thousand were incurred to conduct treatability studies and for design. Annual operating costs have been approximately \$800 thousand. To date, the OU 1 water treatment facility has treated approximately 2,730,000 gallons of ground water. Despite the implementation of the IM/IRA, the water quality data from the collection well continues to indicate elevated levels of VOCs, primarily PCE and TCE (EG&G 1995).

Ground water collected by the French drain and the extraction well is treated using an ultraviolet (UV)/peroxide process for the destruction of VOCs and an ion-exchange system to remove inorganics, metals and uranium. The cost to operate this facility is approximately \$200 thousand per quarter. These costs include chemical purchases, spare parts, labor, preparation of reports, and are virtually independent of the volume of water treated.

The pumping of water from the extraction well to the French drain was discontinued on September 29, 1994 per DOE direction. An alternate method of accumulating the extraction well water, trucking the water daily to Bldg 891, was implemented on November 11, 1994. The purpose for changing the method for collection of water was to better quantify and qualify the water coming

from the French drain and the extraction well. This involved the redesign of the extraction well piping to accommodate transferring water into a portable tanker and the procurement of a tanker/trailer with the proper connections. The extraction well is pumped daily until the remaining water table in the bottom of the well is approximately 0.5 feet. This level is reached in less than 1 hour and results in approximately 303 L (80 gallons) of water being collected per day.  
 $= 0.056 \text{ g/min}$

The extraction well was located in IHSS 119.1 near the highest known concentration of contaminants found in OU 1. However, since the Phase III RFI/RI Report had not been completed at the time of construction of the IM/IRA, the nature and extent of contamination was not fully understood. For this reason, it is possible that residual DNAPL could have been contacted during installation of the extraction well. This would have provided a conduit for the DNAPL source to migrate to the bedrock via the well casing (Cherry, 1994). The OU 1 RFI/RI, however, did not identify contamination by VOCs in the bedrock geologic system known as the Lower Hydrostratigraphic Unit (LHSU).

## 4.2 Review of Hydraulic Parameters and Geohydrology of the OU 1 Area

The RFI/RI and previous geohydrologic investigations have indicated that two hydrostratigraphic units (HSUs) are present at OU 1 and for most of RFETS. These consist of an upper HSU (UHSU) and a lower HSU (LHSU), although the RFI/RI indicates that the boundary between the two is difficult to define (DOE 1994). The UHSU consists of the saturated portion of unconsolidated surficial material, weathered claystones, including slump block, and several discontinuous subcropping sandstone bodies. All UHSU ground water occurs under unconfined conditions and has been generally referred to as alluvial/colluvial ground water. The LHSU comprises the water bearing formations below the UHSU and is composed chiefly of Cretaceous claystones and discontinuous beds of siltstone and sandstone. Sandy and silty layers within the LHSU are water bearing and can be confined or unconfined (DOE 1994). The specific hydraulic parameters for both the Lower and Upper HSU are listed in Table 4.1. The hydraulic conductivity in the alluvium/colluvium (UHSU) is relatively low, ranging from  $3 \times 10^{-3}$  to  $9 \times 10^{-7}$  cm/s and the average darcian velocity is 0.058 m/d.

The ground water in the UHSU does not exist or move as it would within a typical continuous, homogeneous, shallow aquifer system because of the lensing characteristics of the sedimentary beds, the movement restriction caused by the difference in hydraulic conductivities between clay and claystones and the coarse-grained unconsolidated materials, and the low vertical permeability between the UHSU and the LHSU. Little ground water exists in the UHSU bedrock materials,

Table 4-1 Hydraulic Parameters of the Upper and Lower Hydrostratigraphic Units at OU 1

	Back-Pressure Permeability	Grain Size/Lithology	Moisture Content (%)	Hydraulic Conductivity (cm/s)	Transmissivity (cm <sup>2</sup> /s)	Average Darcian Velocity (cm/s)	Effective Porosity (%)
UHSU	Unconsolidated Material, Bedrock	Sand to Clay, varying amounts of Gravel	8 -- 26	3E-3 to 9E-7	3.1	0.058 m/d	5 -- 10
LHSU	Bedrock Claystones, Siltstones, and Silty Sandstones	Siltstones with varying amounts of Sand and Clay	12 -- 15	3E-5 to 5E-7	N/A	N/A	N/A

although there is occasionally a small amount of seepage in slump glide planes. The low seepage indicates that ground water may preferentially reside in the potentially higher permeability glide planes, fractures, or disturbed materials associated with these slumps. The ground water in the LHSU is confined, although locally there are indications that ground water may exist under unconfined conditions. Higher conductivity bedrock sandstone channels transmit water within the LHSU. A conceptual model of ground water at OU 1 would resemble a network of paleochannels in the subsurface where ground water in beds or zones of relatively high permeability are separated by barriers of bedrock and low permeability sediments and flow down-gradient to a discharge point.

The UHSU at the central part of OU 1, near the extraction well, consists of both saturated and unsaturated regions. There is a reduced volume of ground water in this area, as compared to the rest of the UHSU. These saturated and unsaturated regions essentially break up continuous flow in the aquifer and would cause reduced flow gradients where saturated regions do exist.

All of the organic contaminants detected in ground water at IHSS 119 1 are chlorinated solvents that can be classified as DNAPLs. They include carbon tetrachloride, 1,1,1-trichloroethane, 1,1-dichloroethene, tetrachloroethene, and trichloroethylene. Presence of DNAPL is evident in the ground water chemistry and data from the RFI/RI has suggested that a small residual source is present below the ground water table (DOE, 1994). Near the extraction well, there are also high levels of VOCs in the soil gas, which is indicative of residual DNAPL. Wells located over 100 feet down-gradient from the IHSS show much lower levels of DNAPL as a dissolved phase in ground water, possibly indicating the dilution of a ground water plume originating from the DNAPL source near the extraction well. Recent modeling and data interpretation has indicated that the volume of the DNAPL source is approximately 30 L with approximately 4,750 m<sup>3</sup> of aquifer (bulk volume) contaminated by a dissolved plume extending from the residual source (DOE 1995).

#### **4.3 Evaluation of the OU 1 IM/IRA Extraction Well**

NRC (1994) presents and outlines approximations to evaluate the effectiveness of a pump-and-treat operation using known geohydrologic parameters and data concerning the nature and extent of contamination. An evaluation of the potential effectiveness of the extraction well and the pump-and-treat operation at the OU 1 IM/IRA can be estimated with data from the RFI/RI (DOE 1994).

A simple calculation can be made to estimate the amount of time required to extract 1 pore volume equaling the volume of the contaminated plume at OU 1. The calculation assumes that the OU 1

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extraction well would be used to extract the contaminated ground water at 80 gal/d (303 L/d) and that the contaminant plume extends into only 4,750 m<sup>3</sup> of aquifer (this volume is estimated defining the edge of the plume at 80 ppb, it essentially could be much larger) The calculation further assumes that the effective porosity of the aquifer is 0.10

$$4,758 \text{ m}^3 \times 1000 \text{ L/m}^3 = 4,758,000 \text{ L of Aquifer (Bulk Volume)}$$

$$4,758,000 \text{ L} \times 0.10 = 475,800 \text{ L of Contaminated Water in the Plume}$$

$$475,800 \text{ L} / 303 \text{ L/d} = 1570 \text{ Days} = 4.3 \text{ Years}$$

The purpose of this calculation is not to estimate clean up time but to simply illustrate the geohydrologic conditions at OU 1 and in much of the Rocky Flats Alluvium/Colluvium (RFA) This calculation does not illustrate an accurate time for clean up of the aquifer system because the calculation does not account for the factors previously discussed regarding residual DNAPL acting as an almost continuous source (see Section 2.0 and Section 3.0) It also does not account for dilution factors caused from clean ground water mixing with the contaminant plume Obviously the extraction of many pore volumes would be required to significantly reduce the mass of residual contaminant

The approximation does demonstrate, however, that nearly four years of continuous pumping are required to simply extract the existing contaminated plume containing dissolved phase DNAPL Based on case studies, it is not recommended that pump-and-treat systems be designed unless the volume of the contaminated plume can be extracted in less than 1 year (NRC 1994) NRC (1994) guidance further suggests that design considerations also be made based on degree of geologic heterogeneities, presence of residual Light or Dense NAPL, and the potential for a contaminant source to leach to the ground water table These are all confounding factors at OU 1 and in the RFA As previously discussed, the geohydrologic parameters at OU 1 are extremely heterogeneous and complicated by very transient conditions and even intermittent saturation It is very difficult to inject or extract large volumes of water because of extremely low hydraulic conductivities and because of low gradients of potential This is why the extraction well easily dewateres a localized area (capture zone) of the aquifer and a large recovery time is required before pumping can be resumed As shown, nearly four years are required to extract 475,800 L (126,000 gallons) of water using the extraction well Furthermore, data from the RFI/RI suggests that approximately 30 L of DNAPL may occur as immobile residual below the water

A additional calculation can be used to estimate the amount of time required for the dissolution of all residual DNAPL mass in a given volume of aquifer For this example, an approximation will

be made to show the dissolution of DNAPL in a small volume of aquifer (1 m<sup>3</sup>) The calculation can be made using OU 1 data and making the following assumptions (1) an effective porosity of 0.10, (2) a ground water flow rate of 0.058 m/d, (3) 30 L of residual DNAPL occurs as TCE (the density of TCE = 1.47 g/cm<sup>3</sup>), (4) a dissolved TCE concentration equal to 10 percent of the maximum aqueous solubility of 1,100 mg/L (this assumed concentration equals 110 ppm and is an order of magnitude higher than those normally observed at the OU 1 extraction well), and (5) the residual DNAPL occurs as immobile globules randomly distributed in 1 m<sup>3</sup> of aquifer

$$\begin{aligned}\text{Total Contaminant Mass} &= 30 \text{ L} / 1 \text{ m}^3 \times 1.47 \text{ g/cm}^3 \times (100 \text{ cm/m})^3 \times 10^{-3} \text{ m}^3 / \text{L} \\ &= 44,100 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Concentration of dissolved TCE} &= 10\% \times 1,100 \text{ mg/L} \\ &= 110 \text{ mg/L}\end{aligned}$$

$$\begin{aligned}\text{Mass flux through the area} &= 0.058 \text{ m/d} \times 1 \text{ m}^2 \times 110 \text{ mg/L} \times 10^{-3} \text{ g/mg} \\ \text{containing residual TCE} &\quad \times 10^3 \text{ L/m}^3 \times 0.10 \\ &= 0.64 \text{ g/d}\end{aligned}$$

$$V = 69 \text{ ft/year}$$

$$\begin{aligned}\text{Time required to dissolve} &= 44,100 \text{ g} / (0.64 \text{ g/d}) \\ \text{residual TCE} &= 68,906 \text{ days} = 188 \text{ years} \\ &\quad 1160.5 \text{ days} = 3.2 \text{ yr.}\end{aligned}$$

This calculation is considered very conservative because it does not take into account the fact that the rate of dissolution of TCE to the ground water will decrease as the size and exposed surface area of the residual decreases. Furthermore, it assumes dissolved concentrations that are an order of magnitude above those being observed in the OU 1 extraction well. Given these two factors, the actual time required to dissolve the residual TCE in this portion of the aquifer would be much longer than 188 years.

## 5.0 Summary and Recommendations

This report was developed for the DOE RFFO, Environmental Restoration Program because recent information published by the National Research Council concerning the use of pump-and-treat technologies for ground water remediation and because of newly published research concerning the behavior of DNAPLs in the subsurface. This paper outlines many of the problems and factors associated with the remediation of DNAPLs in ground water because this type of contamination has been identified at both OU 1, OU 2, and OU 4. The paper used data from the OU 1 IM/IRA to use as a case study, however, it serves as a good example of conditions which may be expected at OU 2 and OU 4 or with other DNAPL contamination at RFETS. Because data from the OU 1 IM/IRA were used as a case study, specific recommendations have been provided below regarding this IM/IRA and its future use.

In summary, DNAPL is an immiscible, non-wetting fluid with respect to water. These properties combine with the natural heterogeneities in the properties of aquifers to make remediation extremely difficult. Residual free-phase DNAPL is held in both porous and fractured media by capillary forces, making it essentially immobile with respect to the hydraulic potentials acting on the flow of ground water. Pump and treat systems can not extract the free-phase residual DNAPL from an aquifer system but only from the ground water containing the dissolved phase of the contaminant. Residual free-phase DNAPL is held in both porous and fractured media by capillary forces, making it essentially immobile with respect to the hydraulic potentials acting on the flow of ground water. Unfortunately, the solubility of most DNAPLs in water is very low and only a very small proportion of the total mass of the contaminant will be present in the dissolved phase. For these reasons, pump-and-treat technologies do not effectively remediate ground water. NRC (1994) reported that of 42 studied Superfund sites using pump-and-treat for the remediation of DNAPL contamination, none had achieved clean up goals.

This report reviews OU 1 geohydrology in relation to the extraction well which is currently operating under an IM/IRA. The geohydrologic parameters at OU 1 are extremely heterogeneous and complicated by intermittent saturation. The alluvial/colluvial ground water does not exist or move as it would within a typical continuous, homogeneous, shallow aquifer system because of the lensing characteristics of the sedimentary beds, the movement restriction caused by the difference in hydraulic conductivities between clay and claystones and the coarse-grained unconsolidated materials, and the low vertical permeability between the UHSU and the LHSU.

Evaluation of the operation of the extraction well at OU 1 has shown that large volumes of water can not be extracted because of extremely low hydraulic conductivities and because of low gradients of potential. This well only pumps 303 L/d (80 gallons) but in doing so, easily dewater a localized area of the aquifer. A large recovery time is required before pumping can be resumed. Given these data and the hydraulic data from the RFI/RI, it was demonstrated that at least 188 years would be required to remove a 30 L source of residual DNAPL at OU 1.

## 5.1 Recommendations

- 1 It is recommended that DOE discontinue operation of the OU 1 extraction well for the following reasons
  - If residual free-phase DNAPL occurs at OU 1, it is trapped as small ganglia or perched in small pools on low-permeability lenses, because the aquifer is extremely heterogeneous, the distribution of this residual is probably extremely complex, this free-phase residual can not be directly extracted by the well.
  - Because of extremely heterogeneous conditions and low hydraulic conductivities, the well can not extract enough water, which contains only dissolved phase DNAPL, to make a significant reduction in the mass present in the system, calculations indicate that several hundred years would be required to remove the contamination in this manner, this rate of remediation does not justify the costs to operate and maintain this well and treat the effluent water.
  - Data from the RFI/RI suggest that the dissolved plume has not currently reached the French Drain, the extraction well does not need to be operated to contain the contaminated plume because the French drain would provide effective containment between the residual source and Woman creek should a dissolved plume migrate over time.
- 2 The site geohydrologic conditions at OU 2 and OU 4 are similar to that of OU 1. Contamination by DNAPLs have been observed in the alluvial/colluvial material of the UHSU. Therefore, pump-and-treat type remedial alternatives is not recommended for any site at RFETS where free-phase DNAPL residual has been observed.

TCE in bedrock well  
down gradient  
French drain

- continue to then  
remove or leave



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